

# PATENT ABSTRACTS OF JAPAN

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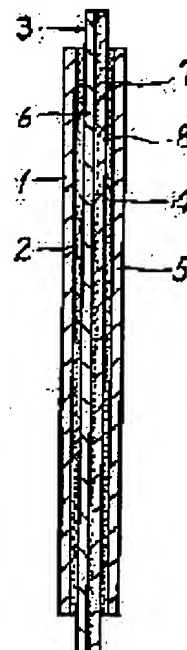
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## (54) POLYMER SOLID ELECTROLYTIC TYPE FUEL CELL

### (57)Abstract:

PURPOSE: To prevent decrease of cell voltage due to crossover of hydrogen gas and oxygen gas in a fuel cell and at the same time make an economical hydrocarbon type ion exchange membrane with small inner resistance usable.

CONSTITUTION: A catalytic layer 7 electrically insulated from a cathode 2 and an anode 4 is formed in an ion exchange membrane 3. Hydrogen gas and oxygen gas crossing over in the ion exchange membrane are reacted each other by the catalytic layer 7 and moved to an opposed pole to suppress decrease of cell voltage and further radicals by which the ion exchange membrane is easily deteriorated are decomposed by the catalytic layer 7. Moreover, the ion exchange membrane 23 is made to be a single membrane and a catalyst metal 26 which is not electrically insulated and a catalyst metal 29 which is electrically insulated may be supported in the cathode 24.



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CLAIMS

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[Claim(s)]

[Claim 1] the charge collector-cathode for cathodes -- the solid polymer electrolyte mold fuel cell characterized by carrying out a laminating to the order of the charge collector for - ion-exchange-membrane-catalyst bed-ion-exchange-membrane-anode-anodes, and insulating said catalyst bed electrically.

[Claim 2] The fuel cell according to claim 1 which the catalyst bed between ion exchange membrane is biasing to the cathode side.

[Claim 3] A laminating is carried out to the order of the \*\* charge collector for charge collector-cathode-ion-exchange-membrane-anode-anodes. a cathode -- It is constituted by the colony where a cathode and/or an anode cover ion exchange resin, and change on catalyst support on the catalyst particle front face which supported the catalyst metal. The solid polymer electrolyte mold fuel cell characterized by having arranged the catalyst particle in the condition of having insulated electrically, in said cathode and/or an anode in the solid polymer electrolyte mold fuel cell of sandwich structure to which each colony and said charge collector were connected electrically.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the solid polymer electrolyte mold fuel cell which lost the crossover of gas, prevented the fall of a cell electrical potential difference, and enabled use of the still cheaper hydrocarbon system ion exchange membrane of low resistance as ion exchange membrane.

[0002]

[The conventional technique and a trouble] Since a solid polymer electrolyte mold fuel cell can take out compact and high current density as compared with a phosphoric acid fuel cell, it attracts attention as a power source for an electric vehicle and spacecrafts. the electrode structure of the conventional fuel cell -- usually -- the object for cathodes -- it has five-layer sandwich structure of a charge collector / cathode / giant-molecule solid electrolyte (ion exchange membrane) / anode / charge collector for anodes. Hydrogen gas and oxygen gas are supplied to this fuel cell, hydrogen gas is made into a cathode pole, counter diffusion of the oxygen gas is made to an anode pole, respectively, and if thickness is thin as a result, anode potential and cathode potential will separate from an original oxidation reduction potential, and will reduce a cell electrical potential difference. The fall of the cell electrical potential difference by the crossover of this gas was conventionally prevented by controlling the osmosis in the film of gas by carrying out thickness of ion exchange membrane to more than constant value (about 100  $\mu\text{m}$ ).

[0003] However, when thickness is thick, there is a fault that resistance will become large and the current density obtained will also become small. Moreover, the radical to which the ion exchange membrane of the conventional fuel cell will generate this by the cathode reaction if a cheap hydrocarbon system ion exchange membrane is used although the sulfonic acid of a stable perfluorocarbon system and the carboxylic-acid type film are used chemically is for preventing carrying out oxidative degradation of the ion exchange membrane, and making it deteriorate. Chemically, since stable perfluorocarbon system ion exchange membrane has large molecular weight, thereby, ion conductivity becomes low and resistance also becomes [ the equivalent (EW) value per unit functional group ] large greatly. When put in another way, even when ion conductivity was not able to reduce resistance using the ion exchange membrane of a cheap high and hydrocarbon system and used which ion exchange membrane of a brown coal-ized hydrogen system and a perfluorocarbon system, in order to reduce resistance, there was a fault that thickness could not be made thin, with the conventional fuel cell.

[0004]

[Objects of the Invention] Although this invention prevents the fall of the cell electrical potential difference produced when the gas in a fuel cell crosses through an ion exchange membrane in view of the above-mentioned trouble and its chemical stability is low as the ion exchange membrane, it is cheap and it aims at offering the solid polymer electrolyte mold fuel cell which also enabled use of the high hydrocarbon system ion exchange membrane of ion conductivity.

[0005]

[Means for Solving the Problem] It is the solid polymer electrolyte mold fuel cell characterized by

carrying out a laminating to the order of the charge collector for - ion-exchange-membrane-catalyst bed-ion-exchange-membrane-anode-anodes, and insulating said catalyst bed electrically. this invention -- the 1st -- the charge collector-cathode for cathodes -- A laminating is carried out to the order of the \*\* charge collector for charge collector-cathode-ion-exchange-membrane-anode-anodes. the 2nd cathode -- It is constituted by the colony where a cathode and/or an anode cover ion exchange resin, and change on catalyst support on the catalyst particle front face which supported the catalyst metal. Each colony and said charge collector are the solid polymer electrolyte mold fuel cells characterized by having arranged the catalyst particle in the condition of having insulated electrically, in said cathode and/or an anode in the solid polymer electrolyte mold fuel cell of the sandwich structure connected electrically.

[0006] Hereafter, this invention is further explained to a detail. The reason for supporting the catalyst metal which formed the catalyst bed electrically insulated between ion exchange membrane by this invention, or was electrically insulated in the electrode structure of a cathode and/or an anode Make the hydrogen gas and oxygen gas which move the inside of ion exchange membrane to the 1st toward hard flow react by this catalyst bed, and it changes into water. It is for controlling that said hydrogen gas and oxygen gas move to a counter electrode, and a cel electrical potential difference decreases. When hydrocarbon system ion exchange membrane is used for the 2nd, it is for changing into the inactive matter the radical which it oxidizes [ radical ] and is easy to degrade said ion exchange membrane that it is easy to generate in a cathode side, and protecting ion exchange membrane. And an internal resistance value can be decreased, without being accompanied by reduction of a cel electrical potential difference instead of the equivalent value currently used conventionally being the ion exchange membrane of the small large perfluorocarbon system of ion conductivity, when an equivalent value enables use of the small large hydrocarbon system ion exchange membrane of ion conductivity.

[0007] Therefore, although ion exchange membrane used for the fuel cell of this invention can be used as the ion exchange membrane of the arbitration which has an ion exchange group and the sulfonic acid of a heat-resistant perfluorocarbon system or carboxylic-acid type ion exchange membrane can also be used, it is desirable to use ion exchange membrane the sulfonic acid of the hydrocarbon system of non-thermal resistance or carboxylic-acid type or the bipolar membrane of a perfluorocarbon system and a hydrocarbon system from economical efficiency and the field of internal resistance reduction. The catalyst particle made to support on the catalyst particle independent of the usual arbitration or proper support can constitute the catalyst bed formed between this ion exchange membrane. In order to contact the hydrogen gas and oxygen gas which cross the inside of an ion exchange membrane as much as possible and to generate water, as for this catalyst bed, it is desirable to form in the shape of film in an ion exchange membrane at the osmosis direction and right angle of gas. For example, predetermined thickness can be made to be able to support with a thermal decomposition method etc. to one side of the ion exchange membrane of two sheets, a catalyst bed can be formed, said ion exchange membrane of two sheets can be unified with a hotpress etc. on both sides of this catalyst bed, and it can consider as the ion exchange membrane of this invention.

[0008] Moreover, since the ion exchange membrane which has said catalyst bed has a possibility that a cathode side may deteriorate by the radical generated by the cathode reaction, from this catalyst bed, a cathode side can use an oxidation-resistant ion exchange membrane with a comparatively large equivalent value from said catalyst bed, and the ion exchange membrane which is inferior to oxidation resistance with a more small equivalent value in order that an anode side may not contact a radical from said catalyst bed can be used, and, thereby, reduction in internal resistance is attained. and since the passing speed of hydrogen is quicker than oxygen, by boiling and arranging the installation location of said catalyst bed from the interface of an ion exchange membrane and a cathode, the effectiveness of preventing a crossover becomes remarkable. Moreover, it is also possible to humidify positively with the water which generates the cathode with which current density is not fully humidified small. The electrode particle which constitutes the electrode of an anode and a cathode should just use the conventional thing which made carbon powder support catalyst metals, such as platinum, as it is. Moreover, the catalyst does not need to be supported by those all and this electrode particle is good also as mixture of a catalyst support particle and a non-supported particle. Furthermore, while covering ion

exchange resin and raising compatibility with ion exchange membrane on this electrode catalyst particle, it is required to make migration of the proton in a catalyst electrode easy.

[0009] And when it locates a catalyst in an electrode in this invention, a catalyst metal is made to support near [ the ] an ion-exchange-resin front face. the cathode manufactured by the usual approach in order to manufacture the fuel cell which made this catalyst metal support -- after immersing the layered product of the \*\* charge collector for charge collector-cathode-ion-exchange-membrane-anode-anodes into water solutions, such as a platinum ammine salt, and carrying out the ion exchange of the exchange group of the ion-exchange resin in said electrode with the cation of platinum, it can return with reducing agents, such as a hydrazine, and a catalyst metal can be made to support on said front face Thus, the supported catalyst metal is electrically insulated from the charge collector for insulation with electric ion exchange resin. Moreover, especially a charge collector is not limited, either but the porous sintering sheet of a carbon paper metallurgy group particle or a carbon metallurgy group mesh can be used preferably. As for this charge collector and said electrode, it is desirable to unify by the hotpress, cold pressing, etc. in advance of secure closing.

[0010] the passage above-mentioned [ these each part material ] -- a cathode -- a laminating is carried out to the order of the \*\* charge collector for charge collector-cathode-ion-exchange-membrane-anode-anodes, and it puts firmly on with hot pressing or the plate for secure closing located in the both sides, and unifies. It is desirable, in addition using the bolt which penetrates the plate for both secure closing and an ion exchange membrane for this secure closing can twist an elastic body etc. around a perimeter, and it can also be fixed. thus, prevention of a fall of the cel electrical potential difference according to the crossover of gas the above-mentioned passage by the catalyst metal in the catalyst bed or electrode with which the fuel cell of this invention constituted exists in ion exchange membrane and thin-film-izing of ion exchange membrane -- it is cheap and use of the high hydrocarbon system ion exchange membrane of ion conductivity and reduction of the internal resistance of ion exchange membrane can be attained.

[0011] The vertical section front view and drawing 2 which show one example of the solid polymer electrolyte mold fuel cell concerning this invention in drawing 1 are the important section enlarged drawing of drawing 1 . This fuel cell consists of the charge collector 1 for anodes, an anode 2, ion exchange membrane 3, a cathode 4, and a charge collector 5 for cathodes sequentially from the left. Said ion exchange membrane 3 is constituted by the cathode side ion exchange membrane 8 which is inferior to ion conductivity and surpasses oxidation resistance from said anode side ion exchange membrane 6 which exists so that this catalyst bed 7 may be inserted with the catalyst bed 7 formed all over one side of the anode side ion exchange membrane 6 which is heavy-gage, surpasses ion conductivity comparatively, and is inferior to oxidation resistance, and this anode side ion exchange membrane 6, and said anode side ion exchange membrane 6. Said cathode 4 consists of two or more colonies which cover with perfluorocarbon system ion exchange resin 11 1 which made the catalyst metals 9, such as platinum, support, or two or more catalyst particles 10, and change on support, such as a carbon particle, and the opening 12 is formed between these colonies. Said catalyst particle 10 is electrically connected to a charge collector 5 through carbon support, and said catalyst bed 7 is insulated electrically. This catalyst bed 7 promotes the reaction of the hydrogen gas and oxygen gas which exist in the location near a cathode 4, contact the radical which has generated with the cathode 4, change into gas or a hydrocarbon, and protect an ion exchange membrane 3 from an anode 2, and cross the inside of this ion exchange membrane 3, changes it into water, and prevents reduction of a cel electrical potential difference.

[0012] The vertical section front view and drawing 4 which show other examples of the solid polymer electrolyte mold fuel cell concerning this invention in drawing 3 are the important section enlarged drawing of drawing 3 R> 3. The fuel cell of illustration consists of the charge collector 21 for anodes, an anode 22, ion exchange membrane 23, a cathode 24, and a charge collector 25 for cathodes sequentially from the left. Said cathode 24 consists of two or more colonies which cover with perfluorocarbon system ion exchange resin 27 1 which made the catalyst metals 25, such as platinum, support, or two or more catalyst particles 26, and change on support, such as a carbon particle, and the opening 28 is

formed between these colonies. Moreover, the catalyst metal 29 is supported near the colony front face of said ion exchange resin 27. Said catalyst particle 26 supported on said support is electrically connected to a charge collector 25 through carbon support, and the catalyst metal 29 supported by said colony front face is insulated electrically. This catalyst metal 29 promotes the reaction of the hydrogen gas and oxygen gas which being arranged in a cathode 24 is desirable, and contact the radical which has generated with the cathode 24, change into gas or a hydrocarbon, and protect an ion exchange membrane 23 from an anode 22, and cross the inside of this ion exchange membrane 23, changes it into water, and prevents reduction of a cell electrical potential difference.

[0013]

[Example] Next, although the example of the fuel cell concerning this invention is indicated, this example does not limit this invention.

[Example 1] After infiltrating a chloroplatinic acid water solution (platinum concentration 150 g / liter) into 10g of carbon powder, pyrolysis processing was performed and the platinum carbon catalyst whose amount of platinum support is 30 % of the weight was prepared. It was immersed in the ion-exchange-resin distribution solution (Nafion solution) of marketing of this carbon catalyst, it dried after that, and the ion-exchange-resin layer was formed in the front face. The amount of support platinum is this catalyst powder An average of 0.3 mg/cm<sup>2</sup> It classified so that it might become, and it was made to re-distribute in alcohol.

[0014] Next, the diameter of 20cm and thickness 360 which function considering this filter paper as a charge collector after making it adhere so that these dispersion liquid may be filtered under weak suction and alcohol may remain said catalyst powder a little on a filter paper with a diameter of 50cm and which carried out water-repellent treatment They are 130 \*\* and 5kg/cm<sup>2</sup> in the carbon paper of mum. The current collection figure electrode with which the hotpress was carried out by the pressure and the anode or the cathode was formed in the field on the other hand was prepared. On the other hand, EW value is 900. The platinum layer was formed in the hydrocarbon system anode with a thickness of 50 micrometers which is ion exchange membrane side ion-exchange-membrane front face by sputtering. Commercial perfluorocarbon system ion-exchange-resin liquid (Nafion liquid) was applied, and the ion exchange membrane containing a catalyst bed of 60 micrometers of total thickness was formed after desiccation at 60 degrees C so that the catalyst bed of this anode side ion exchange membrane might be contacted.

[0015] The laminating of said anode, an ion exchange membrane, and the cathode was carried out, and the bolt was inserted in each bolthole which installs one pair of plates for secure closing which have a bolthole in four corners, and corresponds to the both sides, and it fixed with the nut, and the fuel cell was constituted. That cell electrical potential difference was measured on the following conditions using this fuel cell. That is, it considers as the humidification hydrogen and the non-humidified oxygen of one atmospheric pressure, and the distributed gas to an anode and a cathode is open-circuit voltage and 1 A/cm<sup>2</sup>, respectively. When the electrical potential difference was measured at 80 degrees C, open-circuit voltage was [ the first stage and 10 hour progress back ] about 1020mV. Moreover, current density 1 A/cm<sup>2</sup> A cell electrical potential difference is the first stage and 100. It was after time amount progress and was 620 - 640 mV. These values to a cell electrical potential difference is 100 after a start up. It turns out that it is stable beyond time amount.

[0016]

[The example 1 of a comparison] Except having not formed a catalyst bed, the fuel cell was constituted from the same approach as an example 1, and the cell electrical potential difference was measured on the following conditions by the same conditions as an example 1. the first stage and 100 the cell electrical potential difference after time amount progress -- an open circuit -- respectively -- 820 mV, 810 mV, and current density 1 A/cm<sup>2</sup> \*\*\*\* -- they were 615 mV and 220 mV. By comparing the cell electrical potential difference of an example 1 and the example 1 of a comparison shows that reduction of a cell electrical potential difference considered to originate in the crossover of hydrogen gas and oxygen gas and degradation of the film has arisen notably in the example 1 of a comparison.

[0017]

[Example 2] the cathode constituted like the example 1 of a comparison -- the platinum which is the catalyst metal which is not electrically connected to the platinum and the charge collector which are the catalyst metal which returned the layered product of the \*\* charge collector for charge collector-cathode-ion-exchange-membrane-anode-anodes by the hydrazine after being immersed in the platinum ammine salt water solution (platinum concentration : 0.3g/(l.)), and was electrically connected to the charge collector into the cathode was made to support When the cel electrical potential difference was measured on the same conditions as an example 1 using this fuel cell, open-circuit voltage was [ the first stage and 10 hour progress back ] about 1013mV. Moreover, current density 1 A/cm<sup>2</sup> A cel electrical potential difference is the first stage and 100. It was after time amount progress and was 610 - 655 mV. These values to a cel electrical potential difference is 100 after a start up. It turns out that it is stable beyond time amount.

[0018]

[Effect of the Invention] this invention -- the charge collector-cathode for cathodes -- it is the solid polymer electrolyte mold fuel cell (claim 1) characterized by carrying out a laminating to the order of the charge collector for - ion-exchange-membrane-catalyst bed-ion-exchange-membrane-anode-anodes, and insulating said catalyst bed electrically. Thus, the constituted fuel cell makes the hydrogen gas and oxygen gas which move toward hard flow in the inside of ion exchange membrane react by this catalyst bed, is changed into water, said hydrogen gas and oxygen gas move to a counter electrode, and controls reduction of a cel electrical potential difference, and enables efficient operation. Furthermore, since the radical which is easy to produce degradation of the hydrocarbon system ion exchange membrane which is inferior to oxidation resistance with said catalyst bed can be extinguished, it is cheap and use of a hydrocarbon system ion exchange membrane with small internal resistance is enabled.

[0019] And if the location of said catalyst bed will be carried out soon at the cathode side in ion exchange membrane (claim 2), the fuel cell which has ion exchange membrane with small internal resistance, maintaining the oxidation resistance of the whole ion exchange membrane highly enough by considering as the ion exchange membrane which surpasses ion conductivity although only ion exchange membrane of the thin meat between this catalyst bed and a cathode was used as ion exchange membrane with oxidation resistance and it was inferior to oxidation resistance only in the heavy-gage ion exchange membrane between this catalyst bed and an anode can be offered. Moreover, a catalyst bed cannot be formed between ion exchange membrane, but a catalyst metal can be made to support with the condition of having insulated from the charge collector so that it might expose near the ion-exchange-membrane front face in a cathode and/or an anode in an opening, by this invention (claim 3). Thus, the same effectiveness as the case where it is the fuel cell by which the catalyst bed was formed between ion exchange membrane also with the fuel cell of constituted this invention can be attained.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The vertical section front view showing one example of the solid polymer electrolyte mold fuel cell concerning this invention.

[Drawing 2] The enlarged drawing of the important section of drawing 1 .

[Drawing 3] The vertical section front view showing other examples of the solid polymer electrolyte mold fuel cell concerning this invention.

[Drawing 4] The enlarged drawing of the important section of drawing 3 .

[Description of Notations]

1 ... Charge collector for anodes 2 ... Anode 3 ... Ion exchange membrane 4 ... Cathode 5 ... Charge collector for cathodes 6 ... Anode side ion exchange membrane

7 ... Catalyst bed 8 ... Cathode side ion exchange membrane 9 ... Catalyst metal 10 ... Catalyst particle

11 ... Ion exchange resin 12 ... Opening 21 ... Charge collector for anodes 22 ... Anode 23 ... Ion exchange membrane 24 ... Cathode 25 ... Charge collector for cathodes 26 ... Catalyst particle 27 ... Ion exchange resin 28 ... Opening

29 ... Catalyst metal

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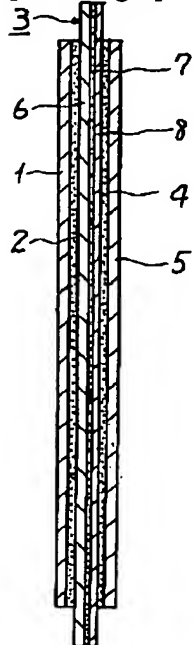
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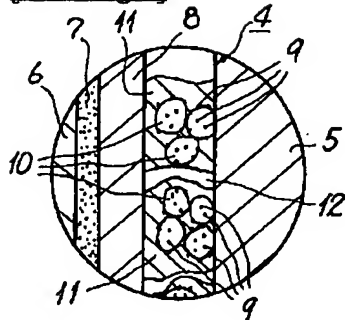
DRAWINGS

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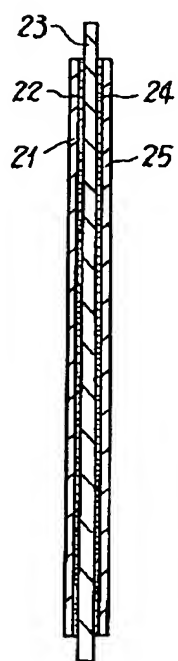
[Drawing 1]



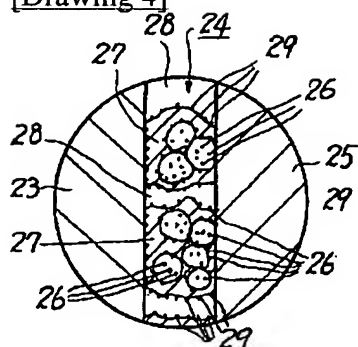
[Drawing 2]



[Drawing 3]



[Drawing 4]



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